Congressional Notification Profile

DE-PS26-02NT41369

UNIVERSITY COAL RESEARCH PROGRAM, CORE PROGRAM
Carnegie Mellon University

Background and Technical Information:
Project Title: "Ab-initio Studies of Coke Formation on Ni Catalysts During Methane Reforming."

This project proposes to use quantum chemistry calculations to clarify the mechanisms that cause carbon (or "coke") and sulfur deposits on nickel catalysts during the reforming of natural gas. The aim is an attempt to find solutions to reduce coke formation on catalysts. Atomically flat and stepped nickel surfaces will be compared to determine why stepped surfaces accumulate more coke. The project will also use low levels of sulfur to reduce coke formation.

A well-known method of producing syngas that can be used for conversion to liquid hydrocarbon fuels is to reform natural gas using nickel catalysts. Coke is carbon that is irreversibly bound to the metal catalyst surface, which stops ability of the catalyst to do its job. A major cost of using this is associated with measures taken to reduce the formation of coke on the catalyst. Results from this study will provide the first direct opportunity to examine surface defect for coke-forming reactions at the atomic scale.

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Funds: FY 2002 $197,779

Ab-initio Studies of Coke Formation on Ni Catalysts During Methane Reforming

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Reforming of natural gas using Ni catalysts represents an important technology for producing syngas that can be used for conversion to liquid hydrocarbon fuels or as a hydrogen source. A major part of the economic investment necessary to practically perform reforming is associated with measures taken to reduce the formation of coke on the Ni catalyst. Coke is carbon that is irreversibly bound to the metal catalyst surface, deactivating the catalyst for reforming.

The atomic-scale mechanisms that lead to coke formation on Ni catalysts during reforming are not well understood, a fact that limits efforts to develop modified catalysts that reduce coke formation under practical conditions. The aim of the proposed work is to use *ab initio* quantum chemistry calculations, specifically plane-wave Density Functional Theory (DFT), to elucidate the fundamental mechanisms of several elementary reactions relevant to coke formation on Ni. Attention will be focused on reactions involving the oxidation of surface carbon by surface oxygen species or adsorbed carbon dioxide and the disproportionation of carbon monoxide, since these reactions are relevant to the build-up (or removal) or net surface carbon. Previous experimental studies have strongly suggested that the reaction rates of these processes are much larger at atomic defect sites such as steps on Ni than on atomically flat planes of Ni. Despite this observation, the limited previous studies of relevant reactions using *ab initio* methods have exclusively examined atomically flat Ni planes such as Ni(111) and Ni(110).

DFT predicts the properties of adsorbed C, O, and CO on these surfaces with quantitative accuracy when compared to experimental data. We have performed a preliminary study that demonstrates that plane-wave DFT is well suited to comparing the binding of C, O, and CO on atomically flat and stepped Ni surfaces. We propose to systematically study the reactions listed above on a series of six single-crystal Ni surfaces that have been chosen to exhibit a broad range of flat and stepped atomic sites: Ni(111), Ni(110), Ni(433), Ni(210), Ni(531), and Ni(532). On each surface we will use plane-wave DFT to determine energetically preferred binding sites and the transition states connecting reactants and products for relevant reactions.

The results from this study will provide the first direct opportunity to examine the atomic-scale mechanisms underlying the high reactivity of surface defect sites for coke-forming reactions. Additional calculations will be performed for surfaces that can be considered chemically modified versions of bare Ni surfaces, namely, partially carbided surfaces and partially sulfided surfaces. Studying partially carbided surfaces will be useful because it will enable us to connect our studies of reactive events involving the deposition of isolated surface carbon atoms to the surface coking that occurs on much larger length scales in practical reforming catalysis. Sulfided Ni catalysts are known experimentally to exhibit greatly reduced coking rates relative to bare Ni catalysts. We will examine whether very low levels of surface sulfur could be used to block highly reactive sites for coke-forming reactions. Examining surface sulfur is also important because sulfur is a ubiquitous trace contaminant in practical natural gas streams.